

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
4 April 2002 (04.04.2002)

PCT

(10) International Publication Number
WO 02/26859 A1

(51) International Patent Classification: C08G 61/10,
H05B 33/14, C07C 211/56

Greenwich House, Madingley Rise, Madingley Road,
Cambridge CB3 0TX (GB).

(21) International Application Number: PCT/GB01/04281

(74) Agents: DANIELS, Jeffrey, Nicholas et al.; Page White
& Farrer, 54 Doughty Street, London WC1N 2LS (GB).

(22) International Filing Date:

25 September 2001 (25.09.2001)

(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI,
SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU,
ZA, ZW.

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

0023539.0	26 September 2000 (26.09.2000)	GB
0028126.1	17 November 2000 (17.11.2000)	GB
60/265,018	30 January 2001 (30.01.2001)	US

(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,
CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD,
TG).

(71) Applicant (for all designated States except US): CAM-
BRIDGE DISPLAY TECHNOLOGY LIMITED
[GB/GB]; Greenwich House, Madingley Rise, Madingley
Road, Cambridge CB3 0TX (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): TOWNS, Carl,
Robert [GB/GB]; c/o Cambridge Display Technology
Limited, Greenwich House, Madingley Rise, Madingley
Road, Cambridge CB3 0TX (GB). MCKIERNAN, Mary,
Joyce [GB/GB]; c/o Cambridge Display Technology
Limited, Greenwich House, Madingley Rise, Madingley
Road, Cambridge CB3 0TX (GB). O'DELL, Richard
[GB/GB]; c/o Cambridge Display Technology Limited,

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/26859 A1

(54) Title: POLYMER AND USES THEREOF

(57) Abstract: A polymer comprising a region having a conjugated backbone capable of transporting negative charge carriers, which region comprises a plurality of repeat units each comprising a core group which comprises an [Ar'] group substituted with at least one pendant group X and the [Ar'] groups form at least a part of the backbone, wherein each Ar' comprises an aromatic or heteroaromatic group and each X comprises NAr₂ in which each Ar is the same or different and independently comprises a substituted or unsubstituted aromatic or heteroaromatic group and N is conjugated with the backbone.

POLYMER AND USES THEREOF

The present invention relates to an organic polymer and uses thereof such as in an optical device.

A typical device for emitting light will comprise an anode electrode, a cathode electrode and a light-emissive layer located between the electrodes. Holes and electrons that are injected from the electrodes recombine radiatively in the light-emissive layer. Organic electroluminescent devices are known which employ an organic material for light-emission. For example, WO 90/13148 describes such a device comprising a semiconductor layer comprising a polymer film which comprises at least one conjugated polymer situated between electrodes. The polymer film in this case comprises a poly(para-phenylene vinylene) film which is capable of light emission when electrons and holes are injected therein.

Known device structures also may have an electron transport layer situated between the cathode and the light-emissive layer. This provides an intermediate energy level which helps the electrons injected from the cathode to reach the LUMO (lowest unoccupied molecular orbital) level of the material constituting the light-emissive layer. Suitably, the electron transporting layer has a LUMO energy level between the LUMO energy levels of the cathode and the light-emissive layer. A device including an electron transport layer is disclosed in, for example, J. App. Phys., 1996, 79(11), pg. 8808-8814 and references therein.

Similarly, known device structures also may have a hole transport layer situated between the anode and the light-emissive layer. Devices disclosed in Applied Physics Letters, 51, 913-915 (1987) consist of a hole transport layer of an

aromatic diamine and an emissive layer of 8-hydroxyquinoline aluminium. ITO is used as the hole injecting electrode and a magnesium silver alloy as the electron injecting electrode.

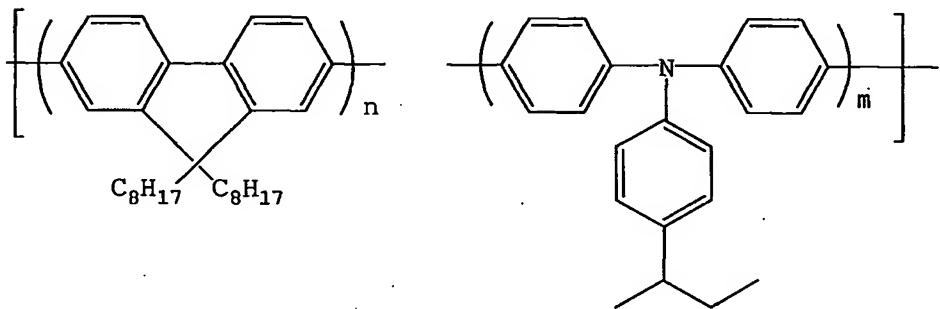
Poly(arylamines) are disclosed in US 5,728,801 as useful charge transport layers in light-emitting diodes. This document further discloses that triarylamines are used as charge transport materials, specifically positive charge transport materials, because they are easily oxidised to the corresponding radical cation. The usefulness of the possibility of using these polymers in film form is discussed in this document.

One disadvantage associated with multiple layer devices is that where the layers are deposited from solution it is difficult to avoid one layer being disrupted when the next is deposited. Problems can arise with voids or material trapped between the increased number of interlayer boundaries.

This problem has been addressed in the prior art. One solution has been to use a blend of at least two different materials in any given layer. For example, a blend could comprise one material for transporting positive charge carriers and a second material for transporting negative charge carriers. Such a blend is disclosed in WO99/48160. For example, this document discloses an emissive layer that is a three component mixture of F8 (poly (2,7-(9,9-di-n-octylfluorene) mixed with F8BT (poly (2,7-(9,9-di-n-octylfluorene)-3,6-Benzothiadiazole) in the ratio 19:1 and then that mixture is mixed with TFB (poly (2,7-(9,9-di-n-octylfluorene)-(1,4-phenylene-((4-secbutylphenyl)imino)-1,4-phenylene)) in the ratio 4:1.

A second proposed solution to this problem has been to provide a single material that is capable of transporting negative charge

carriers and that also is capable of (a) transporting positive charge carriers and/or (b) accepting and combining positive and negative charge carriers to generate light. Such a material is known from PCT/GB00/00911. This document discloses an organic polymer having a plurality of regions along the length of the polymer backbone where each region has a bandgap that is distinct from the other regions so that the polymer is capable of performing more than one of the functions mentioned above. One polymer disclosed in this document is shown below:



the ratio of n to m is about 10.

It can be seen that the backbone of the above polymer is not conjugated along its length because the nitrogen atoms in the polymer backbone act as nodes preventing full conjugation and hence, providing a barrier to and preventing efficient transport of negative charge carriers.

It is an aim of the present invention to provide an improved solution to the above problem. Accordingly, the present invention provides a polymer comprising a region having a conjugated backbone capable of transporting negative charge carriers, which region comprises a plurality of repeat units each comprising a core group which comprises an [Ar'] group substituted with at least one pendant group X and the [Ar'] groups form at least a part of the polymer backbone, wherein

each Ar' comprises an aromatic or heteroaromatic group and each X comprises NAr₂ in which each Ar is the same or different and independently comprises a substituted or unsubstituted aromatic or heteroaromatic group and N is conjugated with the polymer backbone.

By conjugated backbone is meant a backbone which possesses a delocalised π -electron system along its length; the delocalised π -electron system confers semiconducting properties to the polymer and gives it the ability to support positive and negative charge carriers with high mobilities along the polymer chain.

The conjugated backbone contains no nodes which provide a barrier to negative charge transport. For the purposes of the present invention such a conjugated backbone may be defined as fully conjugated.

The present polymer preferably consists of a single 'region' or a plurality of 'regions' which perhaps may be separated by a node preventing full conjugation.

Preferably, the region additionally either is capable of transporting positive charge carriers in the polymer or is capable of combining positive and negative charge carriers in the polymer to generate light.

Where the region is capable of accepting and combining positive and negative charge carriers to generate light, it is believed that the polymers will be most useful in generating "blue" light.

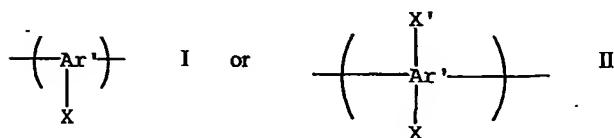
In the defined region of the present polymer, there is no barrier to electron movement in the polymer backbone. Thus, the region is extremely efficient in transporting negative charge carriers. Furthermore, any holes residing on the nitrogen(s) in the NAr_2 group(s) are conjugated with the polymer backbone. In other words, the nitrogen(s) is conjugatively linked to the polymer backbone. This allows facile hole-electron combination in the present polymer as compared with the combination of a hole residing on a nitrogen pendant to the polymer backbone that is non-conjugated with the polymer backbone.

When the present polymer is used in an electroluminescent device, device efficiency is increased and material synthesis is minimised.

In a specific embodiment, the polymer backbone does not contain any nitrogen atoms.

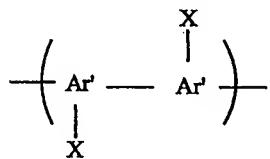
The number of pendant groups X to Ar' is preferably 1 or 2. However, further pendant groups X from Ar' are not excluded. The number of possible pendant groups X predominantly is limited by steric effects.

In the present polymer, it is preferred that the each core group has formula:



where X and X' are the same or different and each independently is as X is defined below.

It is further preferred in the present polymer, in some embodiments, that the region comprises two core groups linked in the polymer backbone by a direct covalent bond. Thus, for example, the region could comprise a group having formula:



where each Ar' and each X is the same or different.

Preferably, X and X' are capable of transporting positive charge carriers in the polymer.

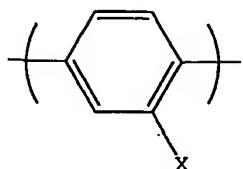
It is preferred in NAr_2 that each Ar comprises a substituted or unsubstituted aryl or heteroaryl group. More preferably, each Ar comprises at least one phenyl or pyridyl group. These groups are preferred for ease of synthesis.

It is envisaged that, usually, each Ar in NAr_2 will be the same.

Referring to Ar', it is preferred that Ar' comprises an aryl or heteroaryl group. This is to further facilitate electron transport along the polymer backbone. It is most preferable that Ar' comprises a phenyl group for this reason.

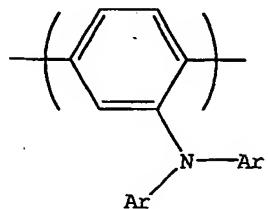
In one embodiment, Ar' does not comprise a fluorene group.

In a first aspect of the present invention, the core group has a formula:



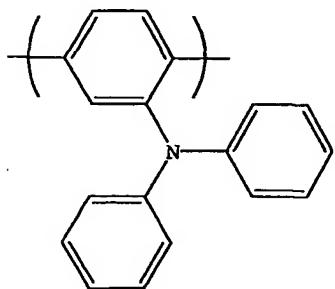
III

More preferably, the core group has a formula:



IV

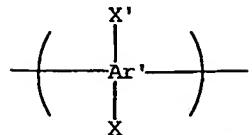
Even more preferably, the core group has a formula:



V

A polymer according to this aspect is envisaged to be extremely useful for transporting negative charge carriers and for accepting and combining positive and negative charge carriers to generate light. However, any polymer according to the present invention may have these properties. In general, it is preferred that where a polymer according to the present invention and particularly the defined region has the capability of accepting and combining positive and negative charge carriers to generate light, the polymer or region will be capable of generating light "blue" light, particularly having a wavelength in the range 410nm to 650nm, preferably about 460nm.

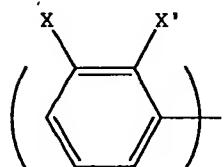
In a second aspect of the present invention, the core group has a formula:



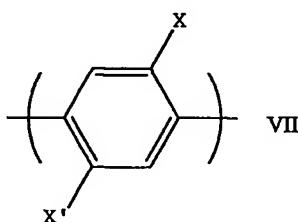
II

It is preferred that X and X' are ortho or para to one another. This enables very efficient transportation of holes within the defined region of the polymer.

According to this second aspect of the present invention, it is preferred that the core group has a formula:

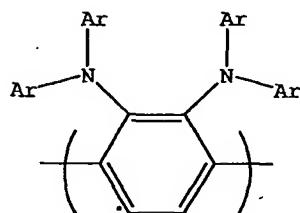


VI or

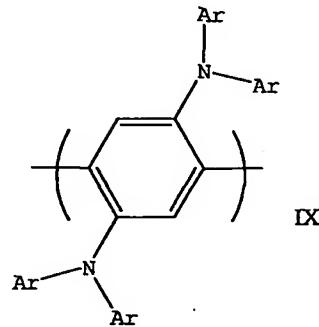


VII

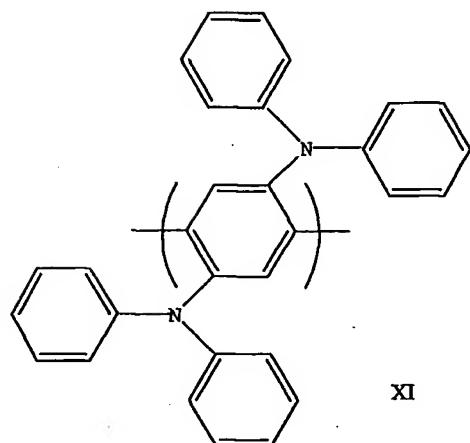
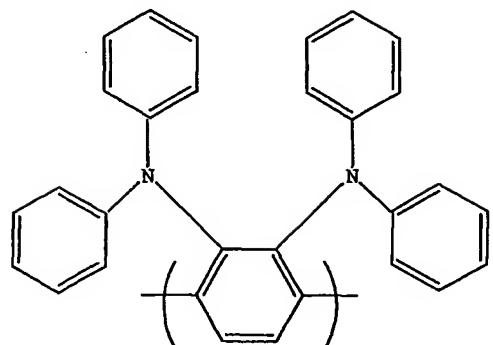
More preferably, the core group has a formula:



VIII or

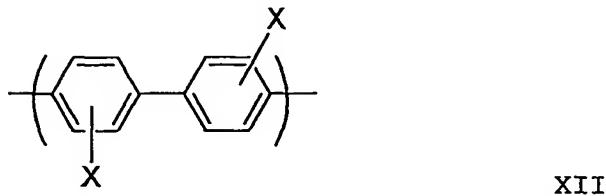


Even more preferably, the core group has a formula:

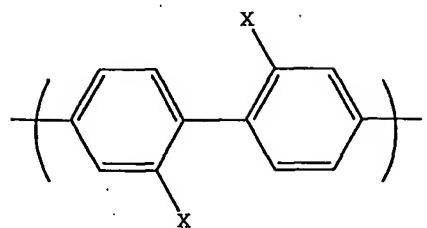


It should be understood that the pendant phenyl groups shown in the above formulae may be substituted or unsubstituted. Possible substituents would include an alkyl, aryl, arylalkyl, alkylaryl, alkoxy, aryloxy, or haloalkyl group, in particular CF_3 .

The present inventors have found that much improved hole transport in the defined region of the present polymer can be achieved when the core group is a bis(triaryl)amine, particularly a para-bis(triaryl)amine. Particularly the core group may have a formula:

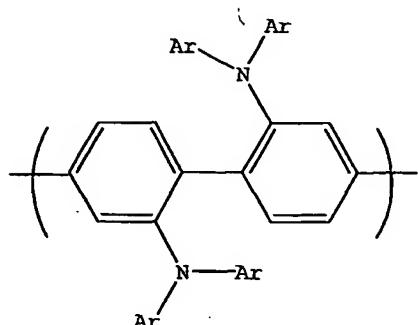


For example:



XIII

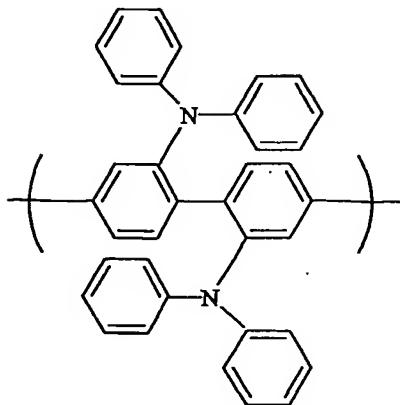
More preferably, for further improving hole transport in the polymer, the core group is ortho-bis(triaryl)amine and preferably has formula:



XIV

Arylamino substituted biphenyls (i.e. "amine" units) also are preferred.

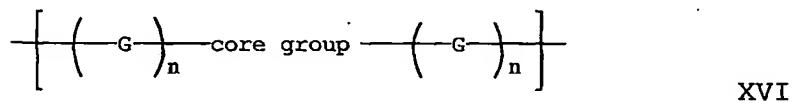
Even more preferably, the core group has a formula (which is substituted or unsubstituted):



XV

In the present polymer, it is preferred that the repeat unit comprises one or more groups G in the polymer backbone in addition to the core group. Each G may be the same or different and each independently comprises a substituted or unsubstituted aromatic or heteroaromatic group.

Preferably, when the repeat unit comprises one or more G groups, the repeat unit will have a formula:



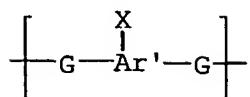
where $0 \leq n \leq 5$. Preferably, $n = 1$ or 2 .

For the same reasons as discussed above in relation to Ar' , it is preferred that each G independently comprises a substituted or unsubstituted aryl or heteroaryl group. Preferred G groups include thienyl, phenyl, pyridyl, furanThese groups contribute to the extent of conjugation in the defined region and, thus, can be used to at least partially control the bandgap of the polymer and to facilitate electron transport along the polymer backbone. More preferable G groups include thienyl and phenyl groups.

Where the repeat unit or region comprises one or more G groups, a preferred repeat unit or region may comprise a group having a formula:

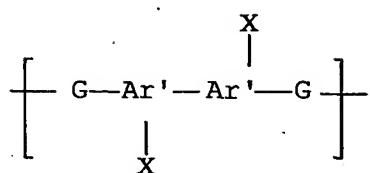


for example



XVIII

or



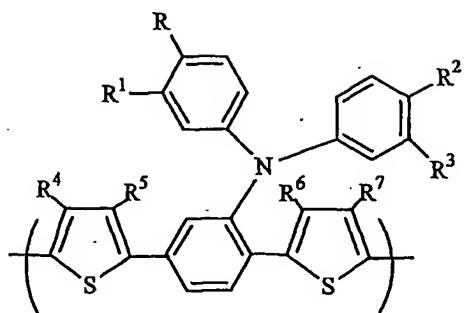
XIX

Preferably, in formula XVIII or formula XIX, Ar' and X are as defined in any preferred embodiment described above.

In formulae XVII to XIX above, it is preferred that each G is a heteroaromatic group, preferably a substituted or unsubstituted thiophene group. Preferred substituent groups on G include alkyl, alkoxy, aryl and heteroaryl groups.

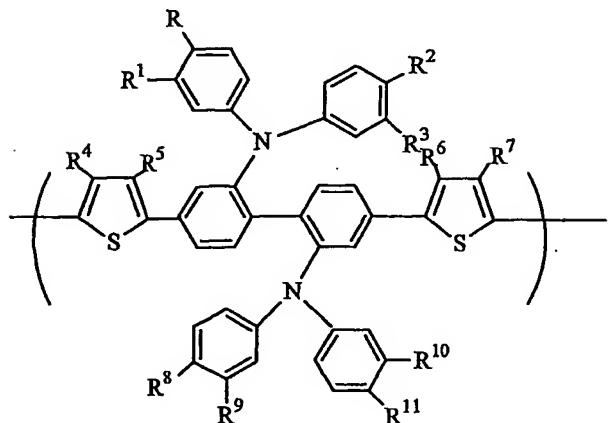
Polymers where a repeat unit or region comprises a group as defined in one of formulae XVII to XIX above, have been found to emit light efficiently when used as an optical device. The introduction of the G groups into these polymers has been found to lower the ionisation potential of the polymer.

By appropriate selection of Ar', X, G and any optional substituents, the bandgap and thus the transport properties and emission colour of the polymer may be tuned. Accordingly, more preferred groups that optionally may be further substituted have formulae:



XX

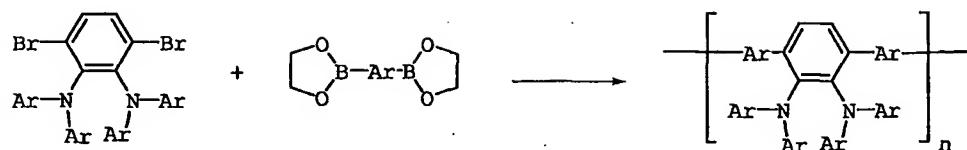
or



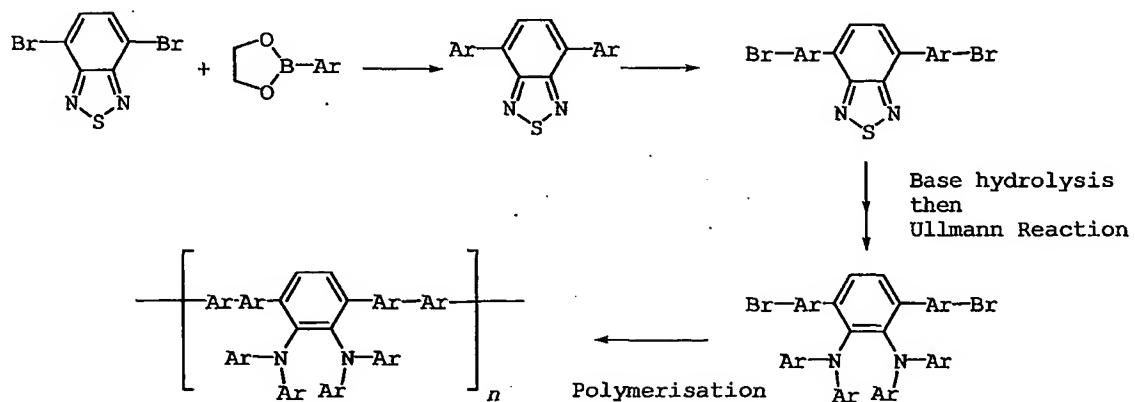
XXI

where R to R¹¹ may be the same or different and each is selected independently from the group consisting of hydrogen; or substituted or unsubstituted alkyl, perfluoroalkyl, alkylaryl, arylalkyl, heteroaryl, aryl, alkoxy, thioalkyl or cyano groups. These are preferred because they are suitable for helping to select the HOMO level and/or for improving solubility of the polymer. More preferably R to R¹¹ independently are selected from the group consisting of hydrogen, substituted or unsubstituted alkyl, aryl and heteroaryl. In this regard ? groups are preferred.

An example of a polymer according to the present invention where the repeat unit comprises 2 G groups where G is Ar is as shown below:



Scheme 2. Metal catalysed polymerisation

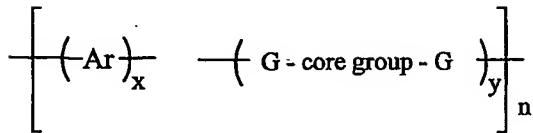


In the above scheme the ortho-bis(triaryl)amine is further derivatised into a trimer unit via a metal catalysed coupling of an aromatic bis-boronic ester with dibromo-benzothiadiazole.

While a polymer according to the present invention includes any polymer such as a homopolymer, copolymer, terpolymer or oligomer, it is preferred that the present polymer comprises a copolymer. In this regard, a copolymer may be defined to have been made from two or more different monomers. If the copolymer is a regular alternating copolymer, the polymer may be defined to have only one repeat unit. In other words, an AB regular alternating polymer which has been made from monomers A and B may be defined to have an AB repeat unit.

Preferred copolymers are 1:1 copolymers as shown in the worked Example.

A further preferred copolymer has the formula:

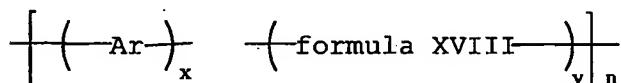


XXII

where $x + y = 1$, and $x \geq 0.3$ and $y \leq 0.7$;

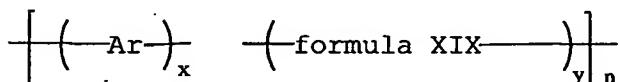
preferably $0.4 \leq x \leq 0.98$ and $0.02 \leq y \leq 0.6$; the core group is as defined in any embodiment above; $2 \leq n \leq 1000$; and the copolymer may be regular alternating, block or random.

Particularly preferred co-polymers have a formula:



XXIII

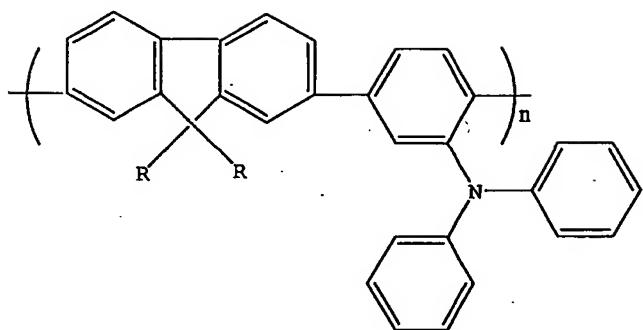
and



XXIV

where x and y and n are as defined in relation to formula XXII. Formulae XVIII and XIX may be defined further in formulae XXIII and XXIV as shown in formulae XX and XXI, respectively. Preferred polymers having formulae XXIII and XXIV have $x=y=0.5$ (i.e. 1:1 copolymers).

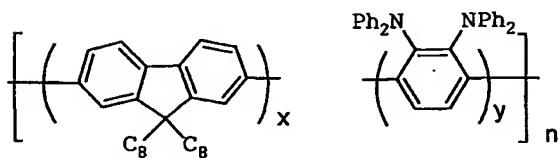
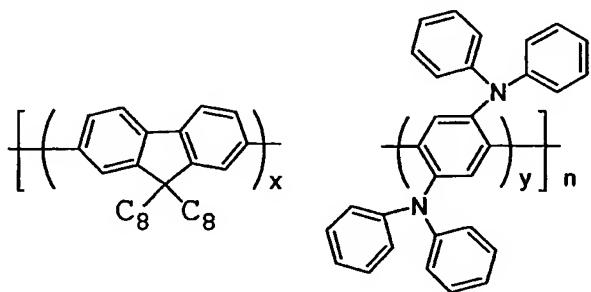
In the present invention, where the present polymer is a copolymer, a preferred comonomer comprises fluorene. An exemplified polymer according to the present invention is shown below:



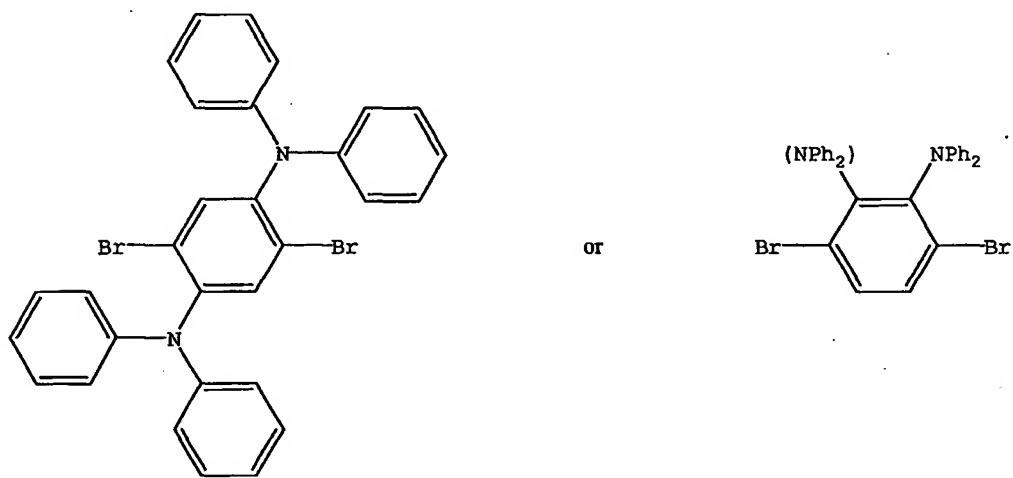
where $2 \leq n \leq 1000$ and R is any suitable substituent group such as alkyl, alkoxy, aryl, arylalkyl, alkylaryl or the like. Preferably, n is about 100.

For any polymer according to the present invention, it is preferred that the degree of polymerisation is in the range of from 2 to 1000, preferably in the range 20 to 200, even more preferably about 100.

Two further polymers according to the present invention are shown below:



where, preferably, $x \geq 0.5$, $y \leq 0.5$ and n is as defined above. Particularly preferred ratios of $x:y$ are 1:1 and approximately 90:10. In the above polymers, for ease of preparation, the fluorene groups would be provided as comonomers together with one of the monomers according to the present invention shown below:



Suitably, the comonomers containing fluorene would contain two reactive boron derivative groups for reaction under suitable polymerisations conditions with the bromine reactive groups on the monomers according to the present invention.

Generally, several different polymerisation methods are known which may be used to manufacture polymers in accordance with the present invention.

One suitable method is disclosed in PCT/GB00/00771. This describes a process for preparing a conjugated polymer, which comprises polymerising in a reaction mixture (a) an aromatic monomer having at least two boron derivative functional groups selected from a boronic acid group, a boronic ester group and a borane group, and an aromatic monomer having at least two

reactive halide functional groups; or (b) an aromatic monomer having one reactive halide functional group and one boron derivative functional group selected from a boronic acid group, a boronic ester group and a borane group, wherein the reaction mixture comprises a catalytic amount of a catalyst suitable for catalysing the polymerisation of the aromatic monomers, and an organic base in an amount sufficient to convert the boron derivative functional groups into $-BX_3$ anionic groups, wherein X is independently selected from the group consisting of F and OH.

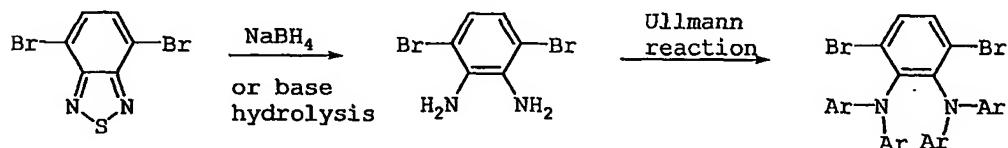
Another polymerisation method is disclosed in US 5,777,070. Commonly, this process is known as "Suzuki Polymerisation". The process involves contacting monomers having two reactive groups selected from boronic acid, C1-C6 boronic acid ester, C1-C6 borane and combinations thereof with aromatic dihalide functional monomers or monomers having one reactive boronic acid, boronic acid, boronic acid ester or boring group and one reactive halide functional group with each other.

A further polymerisation method is known from "Macromolecules", 31, 1099-1103 (1998). The polymerisation reaction involves nickel-mediated coupling of dibromide monomers. This method commonly is known as "Yamamoto Polymerisation".

The present invention also provides a monomer for use in a polymerisation reaction comprising one or more reactive groups and a repeat unit as defined in any aspect above. Preferred reactive groups include halide or reactive boron derivatives groups. In particular, bromine, boronic acid, boronic ester and borane groups are preferred.

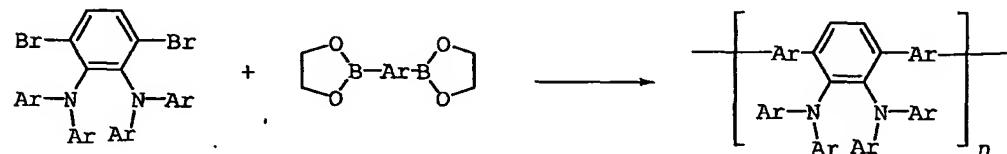
There are a number of approaches for the preparation of a monomer according to the present invention comprising an ortho-bis(triaryl)amine group. Firstly, the monomer could be prepared

by reduction or hydrolysis of dibromo-benzothiadiazole followed by coupling to the diamine of various aromatic species using metal catalysed couplings for example, the modified Ullmann reaction. Such a reaction scheme is shown below:



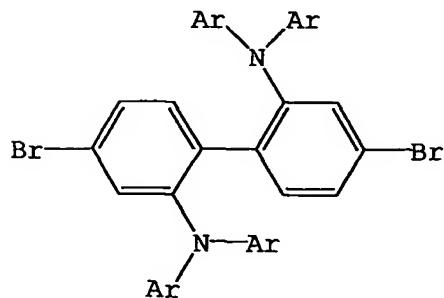
Scheme 1. General synthesis of ortho-bis triaryl amine units

This monomer then can be incorporated into a conjugated polymer as shown below:



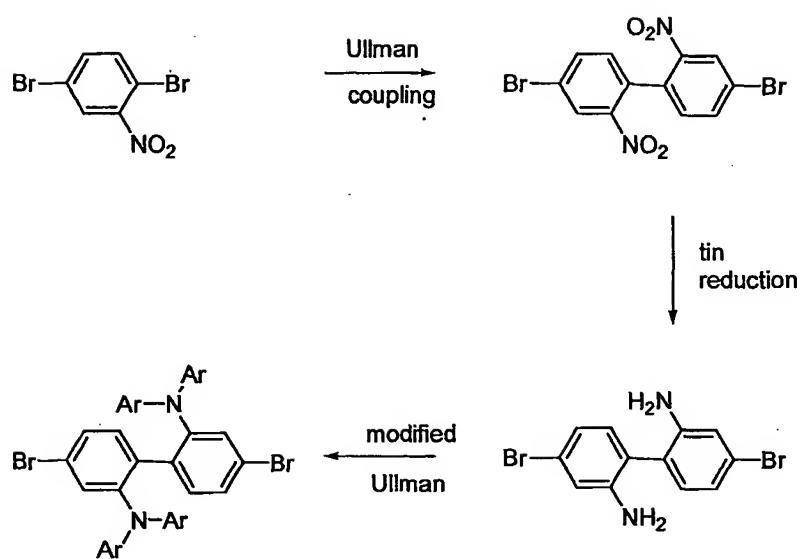
Scheme 2. Metal catalysed polymerisation

In addition to the monomers disclosed above, a further monomer in accordance with the present invention is:

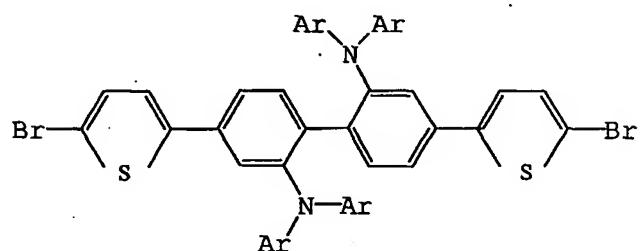


A general reaction scheme for the preparation of this monomer is shown below:

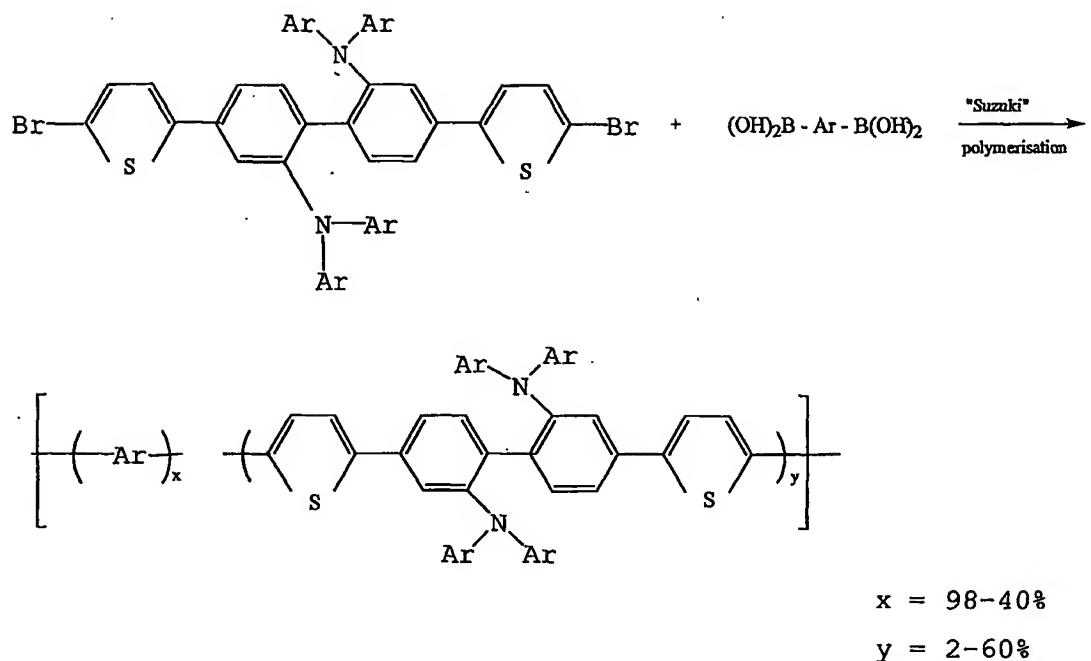
20



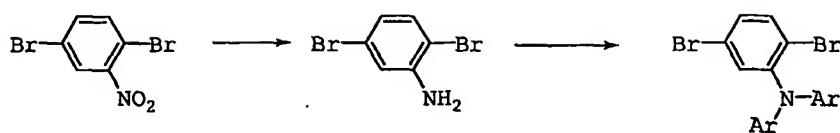
This product may be Stille coupled to a heterocyclic tin derivative to give a desired trimer unit, for example:



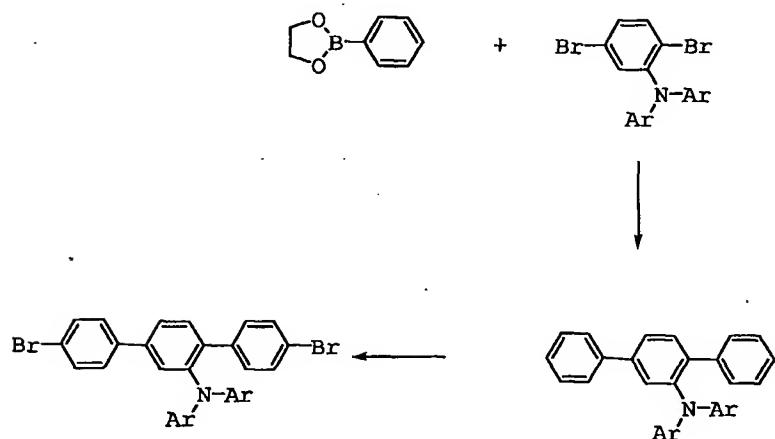
The monomer then can be incorporated into a conjugated polymer as shown below:



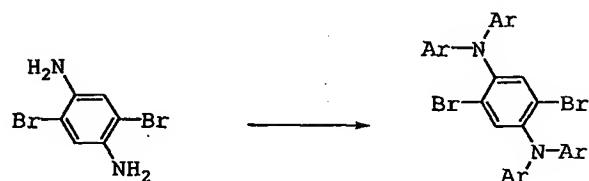
Further reaction schemes for the preparation of monomers according to the present invention are shown below:



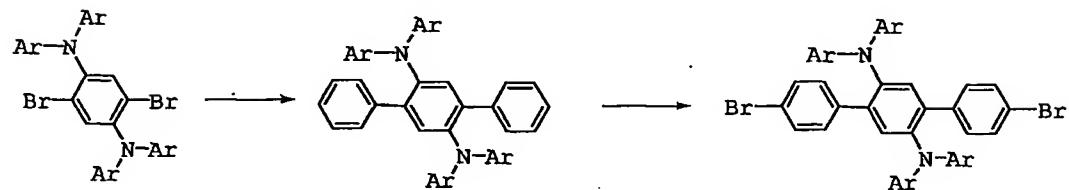
General scheme to orthotriarylamines



General scheme to trimers of orthotriarylamines



General scheme to bis orthotriarylamines



General scheme to trimers of bisorthotriarylamines

The reaction schemes shown above can be modified to prepare a derivative of any monomer according to the present invention shown in the reaction schemes.

The presence of the G groups in the monomer according to the present invention facilitate polymerisation of the monomer. This is because steric hindrance between the X groups comprising NAr_2 and the reactive groups (for example bromine) is reduced.

The present invention further provides the use of a monomer according to the present invention for transporting negative charge carriers in a polymer, for transporting positive charge carriers in a polymer and/or for accepting and combining positive and negative charge carriers to generate light in a polymer.

The use of a polymer according to the present invention as a component in an optical device also is provided. Preferably, the optical device comprises an electroluminescent device.

According to the present invention, there is provided also an optical device for a component therefore which comprises a substrate and a polymer according to the present invention supported on the substrate. Preferably, the optical device comprises an electroluminescent device.

An electroluminescent device according to the present invention may comprise:

a first charge carrier injecting layer for injecting positive charge carriers;

a second charge carrier injecting layer for injecting negative charge carriers;

a light-emissive layer located between the charge carrier injecting layers for accepting and combining positive and negative charge carriers to generate light; and

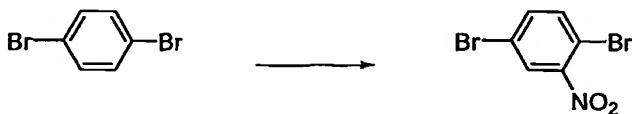
a polymer according to the present invention for transporting negative charge carriers and optionally (a) for transporting positive charge carriers and/or (b) for combining positive and negative charge carriers to generate light and either located between the second charge carrier injecting layer and the light-emissive layer or located in the light-emissive layer.

Finally, the present invention provides a process for preparing a polymer according to the present invention comprising a step of reacting a first monomer which is a monomer according to the present invention with a second monomer that may be the same or different from the first monomer under conditions so as polymerise the monomers. Such conditions will be well known to a person skilled in this art.

The present invention now will be described in more detail:

Examples:

Example 1: Preparation of dibromo nitrobenzene



A cooled (-10 °C) solution of H₂SO₄ (200 mL) was treated with finely ground 1,4-dibromo benzene (94.2 g). the suspension was kept below 10 oC on addition of a cooled solution of (H₂SO₄/HNO₃; 100:160 mL). The reaction mixture was allowed to warm to r.t. with stirring. After 24 h the reaction was quenched by pouring the suspension onto ice. The product precipitated out

and was collected by filtration. The solid product was then vigorously stirred in water (twice) after which the product was filtered and air dried to afford 91.3g (82%). Recrystallisation from methanol was carried out, normal purity after 1 recrystallisation is >98% by HPLC; ^1H NMR (CDCl_3) 7.99 (1H, d, J 2.4), 7.62 (1H, d, J 8.4), 7.57 (1H, dd, J 8.8, 2.0), **Ref: J.A.C.S, 1994, 116, 11723.**

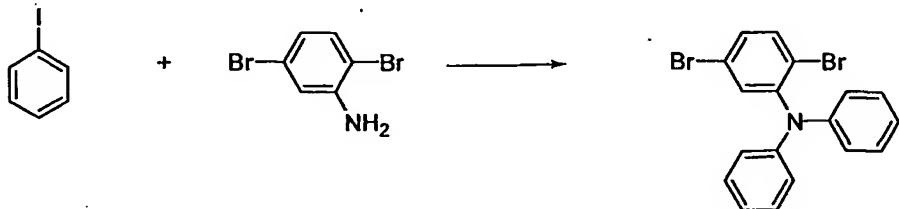
Example 2: Preparation of dibromo aniline



2,5-dibromo nitrobenzene (53.7 g, 24.9 mmol) in EtOH (180 mL) was added slowly (over 0.5 h) to a solution of tin (II) chloride dihydrate (327 g) in cHCl (272 mL). The reaction exotherms to ~ 60 °C after the addition is complete and then subsides. Stirring is continued for a further 18 h and then the product is filtered off. The crude solid is then suspended in EtOH (95%) and treated with NaOH 50% (250 mL) and vigorous stirring is continued for 30 mins. The product is then filtered off, washed with NaOH 50% (2 x 100 mL) and allowed to air dry giving 28.86 g (60% yield); ^1H NMR (CDCl_3) 7.24 (1H, d, J 8.8), 6.89 (1H, d, J 2.0), 6.73 (1H, dd, J 8.4, 2.4), 4.05 (2H, brs); ^{13}C NMR (CDCl_3) 107.968, 118.345, 121.966, 122.378, 133.837, 145.517. **Ref: J.A.C.S, 1994, 116, 11723.**

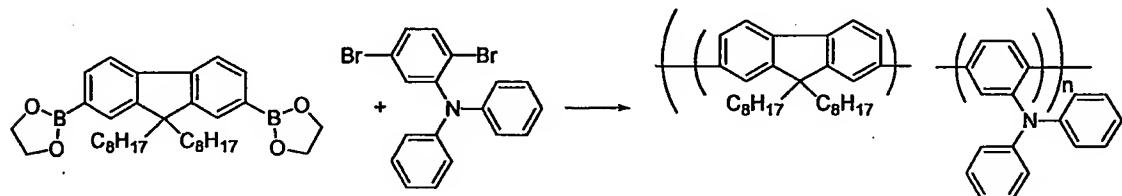
Example 3: Preparation of Amine 1 via the modified Ullmann

A suspension of copper chloride (549 mg, 10%) and 1,10-



phenanthroline (1.0 g, 10. %) in toluene (250 mL) was heated to 130 °C. After 0.5 h, iodobenzene (22 mL, 196.5 mmol), 2, 2-dibromo aniline (13. 9 g, 55.7 mmol) and flaked KOH (21.9 g, 547.5 mmol) was added to the solution and heating resumed at ~ 170 °C for 26h. It was noted that the temperature rose to 185 °C for the last hour. Monitoring by GC_MS revealed de-bromination of product was observed. A standard aqueous work-up, followed by column chromatography (eluting with hexane) and finally recrystallisation from from IPA/Acetone gave 2.58 g (11% yield; 99.9% by HPLC); ¹H nmr (CDCl₃) 7.49 (1H, d, *J* 8.8), 7.34 (1H, d, *J* 2.4), 7.26-7.19 (5H, m), 7.00 (2H, t, *J* 7.6), 6.97 (4H, t, *J* 7.2);

Example 4: Preparation of F8Amine 1 protocol



A suspension of F8-diester (4.46 g, 8.4 mmol), Amine 1 (3.39 g, 8.4 mmol) and tetrakis (triphenyl phosphine) palladium (0) (29 mg) in toluene (42 mL) was de-gased with nitrogen. After 0.5 h, tetraethyl ammonium hydroxide (28 mL) was added to the reaction mixture and the suspension heated to ~115 °C (external temp.). The reaction was end-capped with bromobenzene (1 mL) after 24h. Stirring was maintained at 115 °C for 1h then phenyl boronic acid (1.5 g) was added and stirring continued for a further 1.5 h. Once the reaction mixture had cooled to r.t. the polymer was precipitated into methanol (3 L). The polymer was filtered off and re-dissolved in toluene (250 mL). A solution of dithiocarbamic acid (30 g) in H₂O (120 mL) was added to the toluene solution. The salt mixture was heat to 65 °C for 18 h and then the aqueous layer was removed. The organic phase was passed

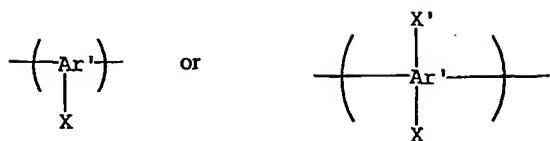
down an alumina/silica column, eluting the polymer with toluene. The toluene was condensed to 250 mL and then precipitated into methanol (4L). The polymer was filtered off and dried thoroughly affording 3.81 g; Mp 80,000.

Example 5: An Optical Device

A suitable device structure is shown in Figure 1. The anode 2 is a layer of transparent indium-tin oxide ("ITO") supported on a glass or plastic substrate 1. The anode 2 layer has a thickness between 1000-2000 Å, usually about 1500 Å. The cathode 5 is a Ca layer having an approximate thickness of 1500 Å. Between the electrodes is a light emissive layer 4 having a thickness up to about 1000 Å. The emissive layer 4, for example, comprises between 0.5 to 30% by weight of the present polymer with the remainder of the emissive layer consisting of hole transport material and/or emissive material. Advantageously, the device includes a hole transport material layer 3 of PEDOT having a thickness of about 1000 Å. Layer 6 is an encapsulant layer of a suitable thickness.

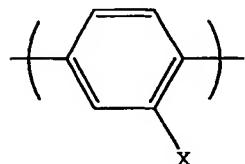
CLAIMS:

1. A polymer comprising a region having a conjugated backbone capable of transporting negative charge carriers, which region comprises a plurality of repeat units each comprising a core group which comprises an $\{ \text{Ar}' \}$ group substituted with at least one pendant group X and the $\{ \text{Ar}' \}$ groups form at least a part of the backbone, wherein each Ar' comprises an aromatic or heteroaromatic group and each X comprises NAr_2 in which each Ar is the same or different and independently comprises a substituted or unsubstituted aromatic or heteroaromatic group and N is conjugated with the backbone.
2. A polymer according to claim 1, wherein each Ar comprises a substituted or unsubstituted aryl or heteroaryl group.
3. A polymer according to claim 2, wherein each Ar comprises at least one phenyl or pyridyl group.
4. A polymer according to any one of the preceding claims wherein the Ar groups in NAr_2 are the same.
5. A polymer according to any one of the preceding claims wherein Ar' comprises an aryl or heteroaryl group.
6. A polymer according to claim 5, wherein Ar' comprises a phenyl group.
7. A polymer according to claim 1, wherein each core group has the formula:

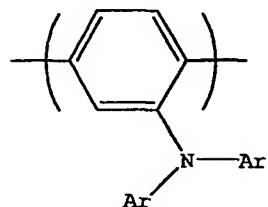


wherein X and X' are the same or different and each is as X is defined in claim 1.

8. A polymer according to claim 7, wherein each core group has the formula:



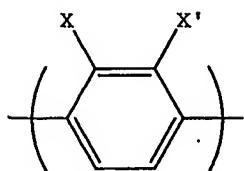
9. A polymer according to claim 8, wherein each core group has the formula:



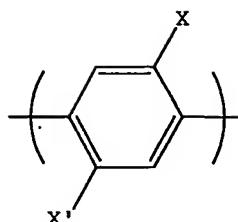
10. A polymer according to claim 7, where X and X' are ortho or para to one another.

11. A polymer according to claim 10, wherein each core group has the formula:

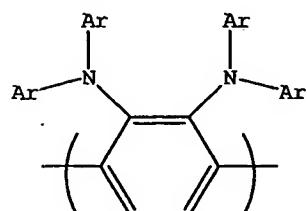
30



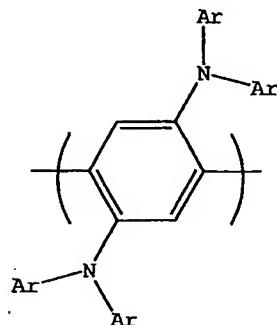
or



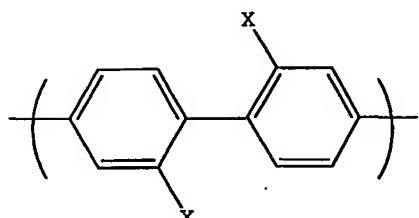
12. A polymer according to claim 11, wherein each core group has the formula:



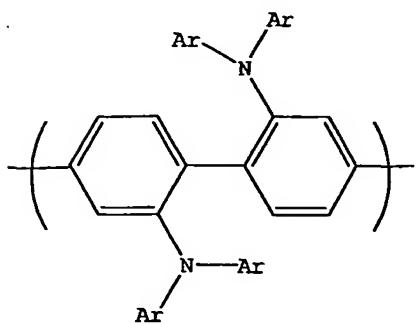
or



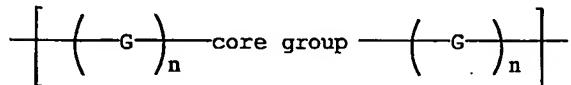
13. A polymer according to claim 10, wherein each core group has the formula:



14. A polymer according to claim 13, wherein each core group has the formula:



15. A polymer according to any one of the preceding claims, wherein the repeat unit further comprises one or more groups G where each G is the same or different and independently comprises a substituted or unsubstituted aromatic or heteroaromatic group so that the repeat unit has a formula:



where $0 \leq n \leq 2$.

16. A polymer according to claim 15 where G is phenyl, thiienyl or pyridyl.

17. A polymer according to claim 16 where G is thiienyl.

18. A polymer according to any one of claims 15 to 17 where $n=1$.

19. A polymer according to any one of the preceding claims, wherein the region is capable of transporting positive charge carriers in the polymer.

20. A polymer according to anyone of the preceding claims, wherein the region is capable of combining positive and negative charge carriers in the polymer to generate light.

21. A polymer according to claim 20, wherein the region is capable of combining positive and negative charge carriers to generate light having a wavelength in the range 410nm to 650nm.

22. A polymer according to any one of the preceding claims, comprising a copolymer.

23. A polymer according to claim 22 further comprising a second repeat unit comprising fluorene.

24. A polymer according to any one of the preceding claims having a degree of polymerisation of about 5.

25. A monomer for use in a polymerisation reaction, comprising one or more reactive groups and a monomeric unit having the structure of a repeat unit as defined in any one of claims 1 to 18.

26. A monomer according to claim 25, comprising two reactive groups where each reactive group independently is halide or a reactive boron derivative group.

27. A process for preparing a polymer comprising a step of reacting a first monomer as defined in claim 25 or 26 with a second monomer that may be the same or different from the first monomer under conditions so as to polymerise the monomers.

28. A process according to claim 27, wherein the second monomer comprises fluorene.

29. An optical device or a component therefor, which comprises a substrate and a polymer according to any one of claims 1 to 24 supported on the substrate.

30. An optical device or a component therefor, according to claim 29, wherein the optical device comprises an electroluminescent device.

31. An optical device according to claim 30, wherein the electroluminescent device comprises:

a first charge carrier injecting layer for injecting positive charge carriers;

a second charge carrier injecting layer for injecting negative charge carriers;

a light-emissive layer located between the charge carrier injecting layers for accepting and combining positive and negative charge carriers to generate light; and

a polymer according to any one of claims 1 to 24 for transporting negative charge carriers and optionally (a) for transporting positive charge carriers and/or (b) for combining positive and negative charge carriers to generate light and either located between the second charge carrier injecting layer and the light-emissive layer or located in the light-emissive layer.

32. Use of a polymer according to any one of claims 1 to 24 as a component in an optical device.

33. Use of a polymer according to claim 32, wherein the optical device comprises an electroluminescent device.

34. Use of a monomer as defined in claims 25 or 26 for transporting negative charge carriers in a polymer.

35. Use of a monomer as defined in claims 25 or 26 for transporting positive charge carriers in a polymer.

36. Use of a monomer as defined in claims 25 or 26 for accepting and combining positive and negative charge carriers to generate light in a polymer.

1/1

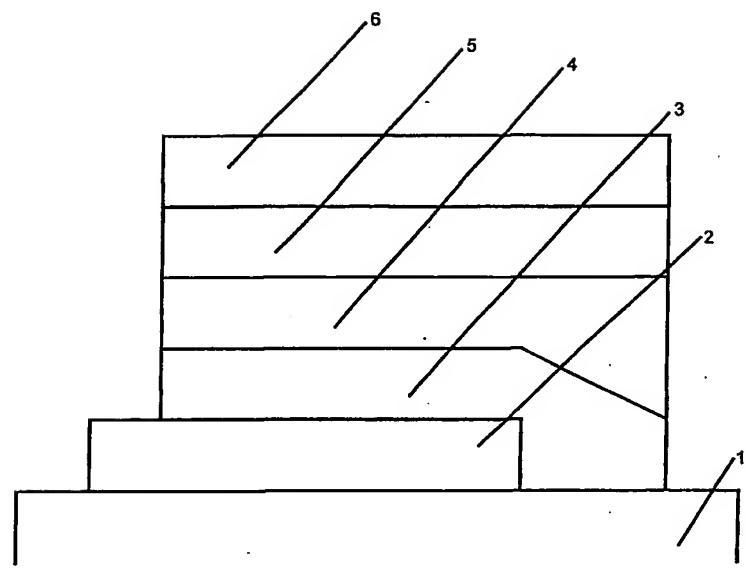


Figure 1

INTERNATIONAL SEARCH REPORT

Internal	Application No
PCT/GB 01/04281	

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C08G61/10 H05B33/14 C07C211/56

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G H05B C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 01 05863 A (STANFORD RES INST INT) 25 January 2001 (2001-01-25) claims	1-36

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

31 January 2002

Date of mailing of the International search report

11/02/2002

Name and mailing address of the ISA
 European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Andriollo, G

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internal	Application No
PCT/GB	01/04281

Patent document cited in search report	Publication date		Patent family member(s)		Publication date
WO 0105863	A 25-01-2001	WO	0105863 A1		25-01-2001
		WO	0106577 A1		25-01-2001
		US	2001053843 A1		20-12-2001